

STUDY ON STRUCTURAL AND THERMAL PROPERTIES OF POLYPROPYLENE SILICA NANOCOMPOSITE FILAMENTS

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ABSTRACT

In this work, the polypropylene filaments containing different proportion of silica nanoparticles were mixed in twin screw extruder and spun through multifilament pilot spinning plant. The morphology of nanocomposite filaments were characterized using scanning electron microscope (SEM), reveal that nano silica powder were uniformly dispersed in polypropylene filament. The presence of silica in polypropylene filament was confirmed by Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). Thermal behavior of the filaments were evaluated by DSC, reveals that incorporation of silica nano particles in polypropylene filament increased the enthalpy (ΔH) and crystallinity % as compared to the pure polypropylene filament. s

KEYWORDS: Polypropylene Filament, Structure, Thermal, Nanocomposite, SiO_2

INTRODUCTION

The nano-structured materials are the most emerging field of science and engineering. It includes metals, metal oxides, silicates, carbon products. These materials can be used either as filler to obtain nano-composite fibers or deposited onto the surface. Metals and metal oxides are important classes of nano-materials [1-3]. In the present time, hybrid polymers, which are the hybrid structure of inorganic-organic nanocomposite materials, are being used to impart the combination of scratch resistance with dirt-repellent effect, high transparency, special barrier properties or antimicrobial function, stiffness with toughness to the material [4-16]. Textile materials play critical role in the manufacture of advanced composite materials in the form of high performance fibres, hybrid yarns and pre-forms. Moreover, these improvements are achieved through conventional processing techniques without any detrimental effects on process ability, appearance, density and aging performance of the matrix.

The dispersion degree of the filler greatly influences the enhancement efficiency. Therefore, in order to meet those excellent properties, it is very important that the average size of fillers must be present in the nanometer-sized ranges with fine particle distribution in the polymer matrix. Silicon dioxide nano particles have shown a great potential as the nano-filler for plastics as well as for fibers [5, 17].

In this work, polypropylene silica nanocomposite filaments were prepared by melt spinning method. The properties of nanocomposite filaments were evaluated in terms of structural and thermal behavior and compared with the filament prepared from pure polypropylene. The chemical transformations have been analyzed using Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and X-ray diffractions (XRD). The change in thermal properties has been evaluated using differential scanning calorimetry (DSC).

MATERIALS AND METHODS

Materials

The polymer used for the manufacturing of nanocomposite filaments was polypropylene homopolymer chips were supplied by one of the reputed company of India. The polymer is fibre grade polymer with 16 MFI (melt flow index). Silica (SiO_2) nano particles with average size less than 100 nm were procured from reputed company of USA, having specifications as mentioned in table 1.

Experimental Methods

Manufacturing of the Polypropylene / SiO_2 nanocomposite filaments were done in two stages: a) mixing of polypropylene (PP) granules with SiO_2 nanoparticles through twin screw extruder; b) extrusion of the nanocomposite filaments by melt spinning on pilot plant.

The SiO_2 nanoparticles were mixed with polypropylene chips in various concentrations of 0.10% (NPP-1), 0.30% (NPP-2), 0.50% (NPP-3), 0.70% (NPP-4), 1.00% (NPP-5), 1.25% (NPP-6) and 1.50% (NPP-7) on the basis of the weight of PP chips. The mixing of the two components was done in twin screw extruder to get homogeneous mixture. The mixture of polypropylene with SiO_2 nanoparticle chips was then fed into the hopper of the optimised spinning conditions on monofilament melt spinning pilot machine. The prepared nanocomposite samples were compared with the sample prepared without SiO_2 nanoparticles, which is considered as control sample (PP) for further investigation.

RESULTS AND DISCUSSIONS

Surface Morphological Analysis through SEM

The SEM micrographs confirm uniform distribution of nanoparticles. Some agglomeration of nano particles can be seen from 1% concentration. This agglomeration may be attributed to the increased concentration of SiO_2 nanoparticles and density difference of polypropylene and SiO_2 . Polypropylene has density of 0.9 gm/cc and SiO_2 has density of 2.65 gm/cc [18]. The amount of agglomeration also increased with the increase in percentage concentration of SiO_2 nanoparticles.

The figure 1(d) shows the cross-sectional view of polypropylene silica nanocomposite filaments of 0.7% concentration of silica nano particles. The distribution of the nanoparticles within the structure has shown good uniformity for all the samples under consideration. Even number of nanoparticles induced within the structure has increased in direct proportion to SiO_2 content. The SEM micrographs show that even with the increase in percentage of SiO_2 content, good particle distribution was obtained.

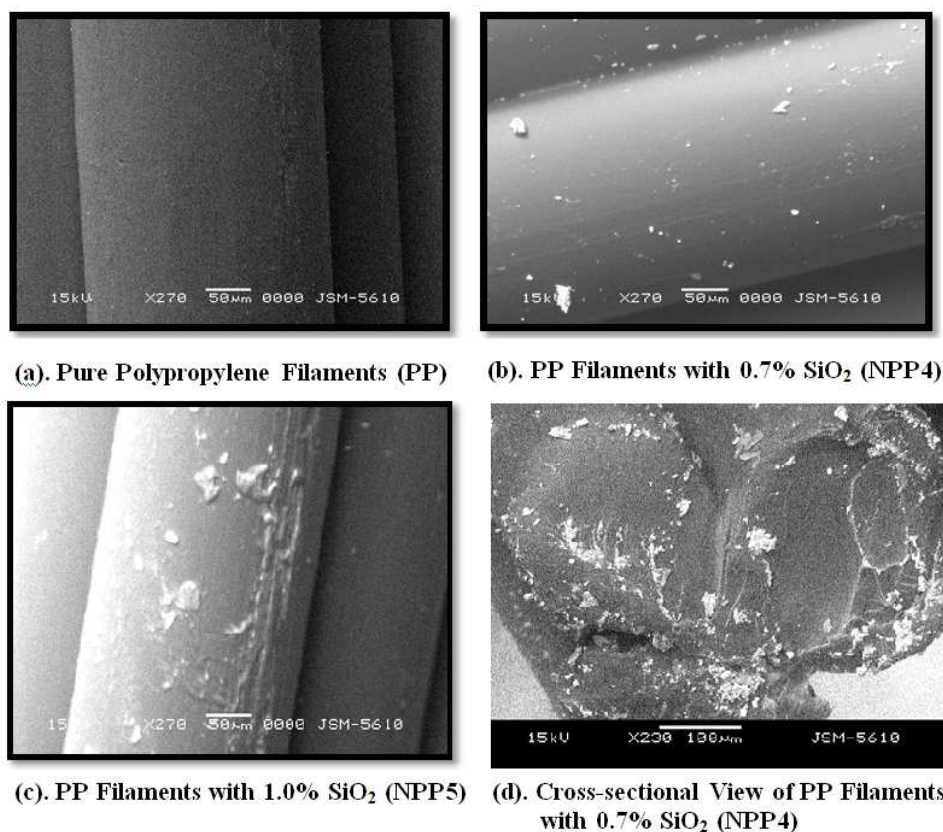


Figure 1: SEM Micrographs of Sample (a) PP, (b, d) NPP4, (c) NPP5

FTIR Spectral Analysis

Figure 2(a) represents the IR characterization absorption peak of pure polypropylene filament, from which it can be seen that the major peaks associated were hydrogen bonded symmetric C-H stretching around 2949 cm⁻¹, asymmetric -CH stretching vibration at 2917 and 2867 cm⁻¹ [19], C-H stretching vibrations [20] at 2837 cm⁻¹, C=O stretching is observed at 1750 cm⁻¹, asymmetrical CH₂ bending [19] scissoring type at 1456 cm⁻¹, symmetrical CH bending [19] at 1376 cm⁻¹, the presence of polypropylene is confirmed at 973 cm⁻¹ which is irrespective of its tacticity, but at 997 and 1166 cm⁻¹ it is confirmed that the tacticity of polypropylene polymer is iso-tactic. Very few O-H stretch and free vibrations peak is observed around 3676 cm⁻¹.

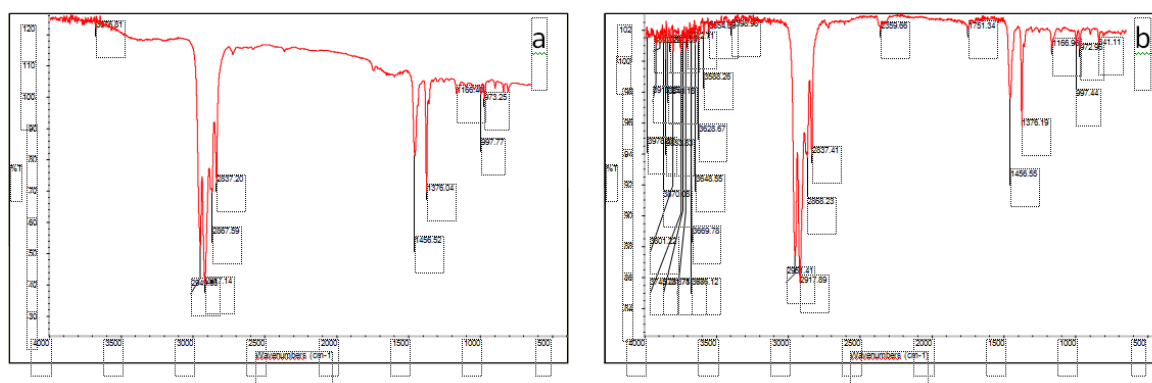


Figure 2: FTIR of (a) Pure Polypropylene Filaments (PP) and (b) PP Filament with 0.70% SiO₂ (NPP4)

Peaks shown by pure polypropylene filaments are identical in polypropylene silica nanocomposite filaments as shown in figure 2(b), additionally the nanocomposite filament shown the peaks of silica at 841 cm^{-1} corresponds to Si-O [21] bending vibration and increased stretching vibrations of O-H in the range of $3500\text{ to }4000\text{ cm}^{-1}$. Intramolecular H-bridges at 2359 cm^{-1} [22] increases as the concentration of silica in polypropylene nanocomposite filament increased, the reason may be silica would be getting bonded with hydrogen at higher concentration. The CO_2 peaks are found at 2340 , 2359 cm^{-1} in the samples from 0.7% concentration of nano silica nanocomposite filaments. The reason could be the oxidation of the methyl group caused the formation of CO_2 and confined to small voids in the Si-O-Si network [23].

X-ray Diffraction Analysis

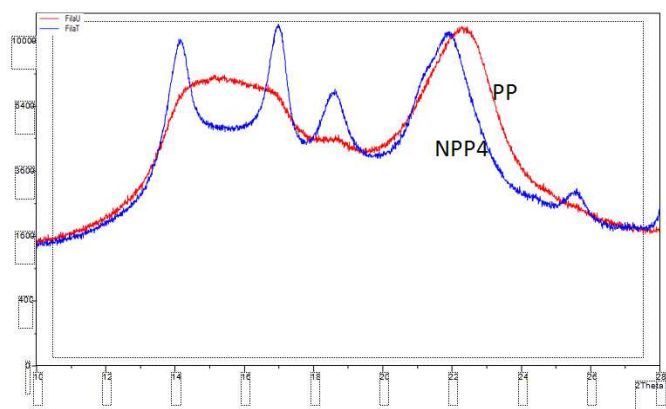


Figure 3: XRD Patterns of PP and NPP4 Samples

The X-ray diffraction patterns were taken on X'pert Pro PANalytical x-ray diffractometer. In the XRD pattern of PP sample in figure 4, only two broad prominent features are observed, which is an indication of a predominantly amorphous structure. The feature at 2θ value of 22.8988° has the highest intensity than other peaks.

Figure 3 also shows the XRD pattern of NPP4 sample, which clearly shows the change in XRD pattern due to addition of silica nano particles. It shows some sharper features with high intensity. Addition of silica nano particles result into enhanced crystallinity, which can be seen from the appearance of multiple peaks in the treated samples. The presence of silica nano particles might be affecting the kinetics of the interaction between the polymer and silica nanoparticles to give better crystallinity. Similar results have been observed by Srisawat, et al. that due to addition of nano silica, the polypropylene crystallinity increases on account of nucleating effect [24]. The 'd' values for the observed diffraction peak of silica is in close agreement with those reported for corresponding standard samples as reported in JCPDS data file no. 84-0384. The peak corresponding to the d-value of 3.9518 \AA is an exact match with the obtained data.

Thermal Analysis

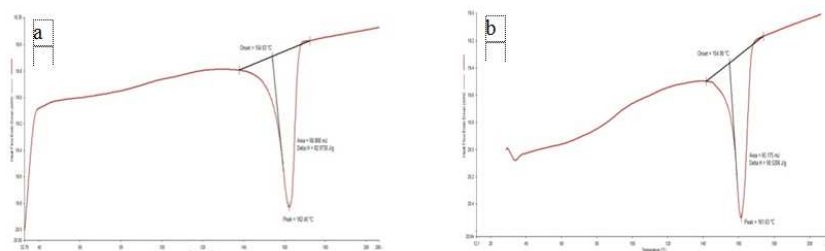


Figure 4: DSC of (a) Pure Polypropylene Filament (PP) and (b) PP with 0.70% SiO_2 Nanoparticles (NPP4)

The thermal analysis was done on DSC 6000, by Perkin Elmer for all the samples. From table 2, the melting temperature of pure polypropylene filament is 162.4°C and there is no significant effect on melting temperature of all the nanocomposite filaments due to addition of silica nano particles. Even though there is agglomeration seen in 1%, 1.25% and 1.5% concentration sample of polypropylene nanocomposite filaments, there is no effect of this agglomeration on melting temperature. It can be also be observed from the table 2 that with increase in SiO₂ nanoparticles concentration the ΔH value (enthalpy) has increased. The increase is in direct proportion to the SiO₂ nanoparticle concentration in polypropylene matrix i.e. upto 1% concentration by 13.57% and thereafter decreased abruptly. The same has led towards the increase in crystallinity value of the nanocomposite filament yarns in the same proportion [25]. Altan et al. [26] had reported that the increase in crystallinity with the increased SiO₂ nanoparticles concentration in polypropylene matrix was mainly attributed to the nucleation role of nanoparticles used. The results obtained in the present research have also followed the same trend. The XRD pattern also showing the increased number of peaks and their intensity, this is an indication of increase in crystallinity.

CONCLUSIONS

Polypropylene chips and silica nano particles were mixed in twin screw extruder and chips were prepared. Pure polypropylene filament and polypropylene-silica nanocomposite filaments were successfully spun on melt spinning pilot machine, the results has been discussed in second part of the study. The presence of silica nano in the prepared composite filament was observed by SEM. The chemical composition of the composite was further confirmed by FTIR spectroscopy. The structure of the prepared composite filament was analyzed by X-ray diffraction technique, which indicates that the structure of the prepared composite filament was crystalline compared to the highly amorphous structure of polypropylene filament prepared without the addition of silica nano. The addition of silica in the polypropylene filament further increases the enthalpy (ΔH) required to melt filament but there was no effect on melting temperature due to loading of nano silica to the polypropylene filament.

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APPENDICES

Table 1: SiO₂ Specifications

Particle Size	< 100 nm
Molecular weight	60.08 Mw
Surface Area	175-225 m ² /g
pH	9
Melting point	>1600°C
Density	2.2 to 2.6 g/ml at 25°C
Bulk density	0.68 ml

Table 2: Effect of SiO₂ Concentration on Thermal Characteristics of PP

Samples	SiO₂ Concentration (%)	Melting Point T_m (°C)	Enthalpy ΔH (J/g)	% Change in Enthalpy	Crystallinity = $\left(\frac{\Delta H}{(1-w_f)\Delta H^*} \right) \times 100$ (%)
CS	0.00	162.40	82.97	0	39.70
NPP1	0.10	161.99	85.50	3.049295	41.03
NPP2	0.30	162.94	87.96	6.014222	42.62
NPP3	0.50	162.97	87.92	5.966012	42.36
NPP4	0.70	161.63	90.52	9.099675	43.75
NPP5	1.00	163.13	94.23	13.57117	45.31
NPP6	1.25	162.45	82.92	-0.06026	40.28
NPP7	1.50	161.42	81.41	-1.8802	38.97

